

Anomalous fast kinetics of lipid monolayer bucklingNaomi Oppenheimer,^{1,*} Haim Diamant,² and Thomas A. Witten¹¹*James Franck Institute, University of Chicago, Chicago, Illinois 60637, USA*²*Raymond & Beverly Sackler School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel*

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We reexamine previous observations of folding kinetics of compressed lipid monolayers in light of the accepted mechanical buckling mechanism recently proposed by L. Pociavsek *et al.* [*Science* **320**, 912 (2008)]. Using simple models, we set conservative limits on (a) the energy released in the mechanical buckling process and (b) the kinetic energy entailed by the observed folding motion. These limits imply a kinetic energy at least 30 times greater than the energy supplied by the buckling instability. We discuss possible extensions of the accepted picture that might resolve this discrepancy.

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I. INTRODUCTION

When a flat thin sheet of material is subjected to increasing pressure, it eventually buckles, crumples, or cracks. By buckling, the sheet releases stress over wavelengths much larger than its thickness. In recent years there has been increasing interest in phenomena, such as crumpling, where the deformation goes from an initial uniform state to a localized region occupying an arbitrarily small fraction of the sample [1]. Monolayers of surface-active molecules (surfactants), adsorbed on a liquid, are found in many systems containing water-air or water-oil interfaces [2]. Such monolayers exhibit a rich variety of collapsed structures under lateral compression, most of which occur on an intermediate scale between the macroscopic one and the molecular thickness of the layer. Fluid monolayers collapse into disks, tubes, or pearls-on-string structures, depending on spontaneous curvature and charge of the lipid monolayer [3]. Like elastic sheets, many solid-like monolayers crack [4,5] or buckle [6] under pressure, yet other solid-like monolayers fail by abrupt buckling into straight, micron-wide folds [7–15] (see Fig. 1 for an example). In addition, liquid-like monolayers may form micron-scale vesicular objects of various shapes [7,16,17] or giant convoluted folds [9,10]. This type of folding is believed to be driven by the interfacial energy gained from the contact across the two sides of the fold [10]. Thus, the failure of surfactant monolayers under lateral pressure displays distinctive mechanical behaviors, which crucially depend on the in-plane rigidity [7,18,19] and viscoelasticity [10]. Lipid monolayers and bilayers are the material of choice for spatial partitioning in living matter, such as cells and compartments within them. These partitions are often observed to fold and wrinkle under stress. In particular, lipid monolayers that model the expanding and contracting sacs in an animal's lung exhibit the abrupt folding signature described in Refs. [20–22].

These puzzling buckling events or “jerks” were the subject of an extensive statistical study in 2006 [13]. DPPG:POPG lipids were spread on the air-water interface of a Langmuir trough and viewed in an optical microscope as the trough was gradually compressed. The micron-sized folds (indicated by the bright line in Fig. 1) cause the entire (15 cm) monolayer to

translate. In most cases, the fold was outside the field of view, but its formation could be inferred by the observed motion of the sheet. The distinctive length and time scale of the jerks have not been explained. Why do the jerks occur over a time scale of about 0.1 s—far from any molecular or apparatus time scales? Why does the motion stop suddenly, before the driving stress is relaxed? Why do the jerks show a robust characteristic displacement of a few microns?

An intriguing hypothesis to explain this micron-length scale was recently proposed by Pociavsek *et al.* [3,14]. These authors recalled that any thin sheet under compression on a liquid substrate buckles at a well-defined wavelength λ . For lipid monolayers, the expected value of λ lies in the micron range. Thus, it is of the same order as the characteristic displacement of the jerk relaxations. These authors also noted that the incipient wrinkles at wavelength λ are unstable against folding, in which the excess wrinkled material from throughout the sample is concentrated into a single loop or fold.

This paper aims to account for the dynamical features of the jerk motion. In Sec. II we argue that the monolayer may be viewed as a broad, thin slab that translates almost rigidly during the jerk motion. In Sec. III we describe how such a slab should respond to horizontal forcing, accounting for progressive viscous entrainment of the fluid subphase. Using this result, combined with experimental observations, we set a lower bound on the kinetic energy of the jerks. We then survey the possible forces that might give rise to this kinetic energy, notably the energy released by folding in the mechanism of Ref. [14]. Even upper limits of this folding energy are far less than the observed kinetic energy. In Sec. IV we discuss effects that might account for this kinetic energy.

II. SYSTEM

For definiteness we focus our study on the jerks analyzed in Ref. [13] and reexamined in Ref. [14]. We begin by reviewing the parameters of this system. The monolayer was a 7:3 mixture of dipalmitoylphosphatidylcholine (DPPC) and dioleoylphosphatidylglycerol (POPG) spread on pure water at room temperature in a 15-cm-long Langmuir trough and viewed in a microscope in a 100- μ m-wide field of view at conventional video frame rates. It is compressed at 0.1 mm/s to a nominal pressure of about 70 mN/m before viewing. The measured pressures are consistent with the slight overpressure

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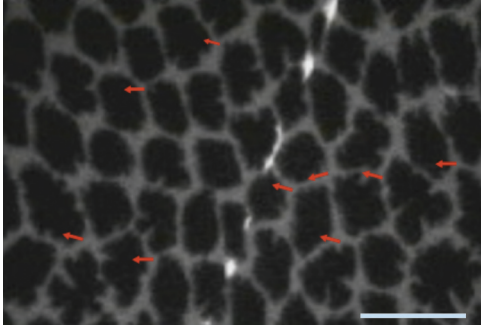


FIG. 1. (Color online) Frame from fluorescence-microscope video of a compressed mixture of DPPG and DOPG lipids, courtesy of the authors of Ref. [13]. Dark domains are the condensed phase; lighter channels are the liquid phase. Bright line is a fold created earlier. Bar indicates $50 \mu\text{m}$. Arrows indicate the displacement during a jerk event.

needed for folding [14,23]. In these conditions this material microphase-separates into a biphasic foam-like pattern of compact patches separated by narrow strips of different composition, visualized by a dilute fluorescent additive. The patches are $15\text{--}25 \mu\text{m}$ in size. The monolayer behaves mechanically as a solid, not a fluid; the jerks move in the direction of the Langmuir barrier motion. Rheological measurements in similar systems showed stress relaxation times of order $10\text{--}10^2 \text{ s}$ [10,24]. The jerks vary statistically in their net displacement Δ and their duration t . No statistical correlations between jerks were observed. The displacements Δ vary from a minimum of about $1.2 \mu\text{m}$ to several times larger, with an average of $2 \mu\text{m}$ [13]. The durations t vary from a minimum of about 0.09 s to a few times longer, where the average is 0.12 s . It has been suggested [13] that the larger jerks are cascades of elementary jerks, with this average Δ and t . In the estimates below, we use these average Δ and t values.

We may simplify our description of the monolayer using three further features. First, the monolayer may be assumed to translate *rigidly* outside the folding region over distances of several cm. It thus entrains substrate fluid over these distances. In principle, compressibility could invalidate this assumption. Compressibility implies that an initial imbalance of membrane stress produces a compressional wave whose speed is given by $c = \sqrt{Y/\rho_s}$, where Y is the two-dimensional uniaxial compression modulus and ρ_s is the mass density per unit area. If forces are applied on a timescale t , the resulting compression or expansion is confined to distances $L \lesssim ct$. Conversely, the compression is negligible and the body moves rigidly if its size L is smaller than about ct . Thus, to show that our monolayer translates rigidly, we must establish that c is sufficiently large.

For our case, the density ρ_s is the density of the material to be accelerated in propagating the wave. Since the monolayer entrains substrate fluid as it moves, the density must take account of this subphase. We may find a lower limit on this c by using a lower limit to the modulus Y and an upper limit for the surface density ρ_s . Accordingly, we estimate Y by neglecting any compressional effects of the subphase. Measurements of the monolayer compression modulus range from 0.1 N/m to several N/m [18,25,26]. We use the conservative estimate of $Y > 0.1 \text{ N/m}$ below. As for the surface density ρ_s , we find an

upper limit by including all the water that might be entrained. As discussed in Sec. III, an upper limit on the entrained density ρ_s is given by $\rho_s < 2\rho\sqrt{\nu t}$, where ρ (10^3 kg/m^3) is the density of the water subphase, and ν ($10^{-6} \text{ m}^2/\text{s}$) is its kinematic viscosity. Thus, in the jerk time of 0.12 s , a local compression can propagate a distance $ct > 0.05 \text{ m}$; i.e., even by our minimal assumption, information from the folding region has reached about half the sample (5 cm) within the jerk time. Thus, we expect only minor effects from compressibility of the sheet. In the calculations to follow, we will assume $L = 5 \text{ cm}$ is the size of the moving sheet.

A second feature of the monolayer is that its compressibility has negligible effect on the energetics of folding. As explained below, the over-pressure p released in the wrinkle-to-fold transition [14] in this system must be smaller than $6 \times 10^{-5} \text{ mN/m}$. Given the large lower-bound modulus Y above, the compressive displacement Δ_{com} in a system of length L is smaller than $Lp/Y < 0.03 \mu\text{m}$. It is, thus, much smaller than the observed displacements Δ . Likewise, the compressive energy released is a small fraction ($p\Delta_{\text{com}}/p\Delta$) of the folding energy.

A third feature of these monolayers is that the longitudinal propagation of the fold tips is much faster than the transverse folding and its accompanying jerk. Within the temporal resolution of Ref. [13] ($\sim 0.03 \text{ s}$) the fold traverses the field of view ($\sim 150 \mu\text{m}$) instantaneously; this sets a lower bound of $\sim 5 \text{ mm/s}$ for its speed. In the system of Ref. [11], two types of longitudinal folds were observed, the slower of which propagated at $\sim 10 \text{ mm/s}$. Comparing these values with the characteristic translation velocity, $10 \mu\text{m/s}$ [13], we see that the requirement is safely fulfilled. These features allow us to consider a simplified two-dimensional problem of a thin elastic sheet moving over a semi-infinite viscous liquid (Fig. 2).

Current understanding [3,14] attributes the jerks to the mechanical buckling or wrinkling instability of any elastic sheet that is floating on a liquid and is under compression [27]. Above a threshold pressure p_c , the sheet distorts, at a cost of bending energy. The wrinkles also produce a net upward and downward displacement of the liquid, thus increasing its gravitational energy. Taking account of these costs, one finds a threshold pressure given by $p_c = 2\sqrt{B\rho g}$, where B is the bending stiffness and g is the acceleration of gravity. The predicted buckling wavelength λ is given by $\lambda = 2\pi[B/(\rho g)]^{1/4}$. This buckling is unstable, leading to a release of the overpressure p_c over a displacement Δ_f comparable to λ . Though p_c is too small to measure directly in our system, it can be estimated either using typical values of B or by inferring B from the observed jerk displacement. Bending stiffness for lipid monolayers like our system are of the order $B \lesssim 10^{-19} \text{ J}$ [28]. This B value implies an upper

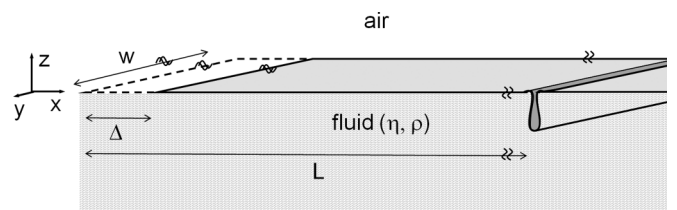


FIG. 2. Schematic view of the system and its parametrization.

bound for p_c : $p_c < 6 \times 10^{-5}$ mN/m. If instead we infer p_c from the observed jerk displacements via $p_c = \rho g \lambda^2 / (2\pi^2) = \rho g \Delta_f^2 / (2\pi^2)$, we obtain values of 2×10^{-6} mN/m, i.e., 30 times smaller than our upper bound [29]. In what follows we will use the more conservative “upper-bound” value of p_c , namely 6×10^{-5} mN/m. There are many forces in the system that exceed this value—the total pressure from the trough, drift flows, flows from faraway jerks, or residual flows from previous jerks. However, these larger pressures lack the central feature needed to explain jerks. The jerks clearly result from an instability, in which a small displacement Δ leads to an increasingly *unbalanced* pressure.

To summarize the above discussion, the sheet is assumed to deform in the x - z plane while remaining uniform along the y axis. It is laterally compressed by a two-dimensional, uniform pressure p . (In the experimental system, p is given by the actual pressure exerted at the boundaries minus the surface tension of the liquid.) Prior to instability, the monolayer remains flat ($h = 0$) and responds to compression by slightly decreasing its actual length. When the pressure exceeds p_c , the monolayer wrinkles or folds out of the x - y plane ($h \neq 0$). Since the pressure p_c produces negligible elastic compression, the total length L is fixed, and the displacement Δ along the x axis is fully accounted for by the wrinkles or folds. The underlying liquid, having viscosity η and mass density ρ , occupies the region $z < h$.

III. DYNAMICS

A. Constant pressure

As noted above, the motion of the sheet depends strongly on the viscous entrainment of the fluid beneath it. In this section, we determine the motion taking account of this entrainment. We begin with a simplified situation. Suppose we control the surface pressure and increase it above the instability pressure, p_c . We further suppose that as the sheet begins to fold, the buckled region is decreasing the pressure by a constant amount p . At this moment the forces on the sheet are unbalanced and it begins to accelerate. In all but the small folding region the sheet is horizontal and its motion is a pure horizontal translation. The flat sheet adjacent to the fold will translate laterally, thus creating a velocity profile $v(z)\hat{x}$ in the underlying liquid. On larger scales, this flow produces circulation of fluid in the sample. We ignore such large scale gestures, since these only increase the kinetic energy and the discrepancy we are discussing. The resulting viscous drag decreases with time, as the velocity profile penetrates deeper into the liquid and its gradient becomes less sharp. We shall assume that the sheet’s velocity is always equal to that of the water immediately beneath it. That is, the fluid obeys a no-slip boundary condition. We examine such assumptions in Sec. IV below. We may neglect the mass of the sheet relative to the much greater mass of the entrained fluid. Thus, the problem is simplified to that of finding the velocity of a half-infinite fluid due to a rigid surface moving with a constant lateral pressure.

The equation of motion for the fluid is

$$\dot{v} = \nu \partial_{zz} v, \quad (1)$$

where ν is the kinematic viscosity given by the ratio of viscosity and density, $\nu = \eta/\rho$, and a dot denotes derivative

with respect to time. The constant stress at $z = 0$ implies a boundary condition of the form

$$\partial_z v|_{z=0} = -\frac{p}{L\eta}. \quad (2)$$

Accompanying it are the condition of vanishing flow far away from the interface,

$$v(z \rightarrow -\infty, t) = 0, \quad (3)$$

and initial conditions of stationarity,

$$\Delta(t = 0) = \dot{\Delta}(t = 0) = v(z, t = 0) = 0. \quad (4)$$

Equations (1) and (2) may be simplified by defining the Laplace transform $\tilde{v}(\omega)$ by $\tilde{v}(\omega) \equiv \int_0^\infty v(t)e^{-\omega t} dt$:

$$\omega \tilde{v}(z, \omega) = \nu \partial_{zz} \tilde{v}(z, \omega), \quad \partial_z \tilde{v}|_{z=0} = -\frac{p}{\eta L \omega}. \quad (5)$$

The solution in Laplace space is

$$\tilde{v}(z, \omega) = \frac{p\sqrt{\nu}}{\eta L \omega^{3/2}} \exp(\sqrt{\omega/\nu} z), \quad (6)$$

and in the time domain,

$$v(z, t) = 2p(\nu t / (\pi L^2 \eta^2))^{1/2} [e^{-\alpha^2} + \alpha(\text{Erf}(\alpha) + 1)], \quad (7)$$

$$\alpha \equiv z / (2\sqrt{\nu t}).$$

The displacement of the sheet is given by integrating the velocity on the surface, $\Delta = \int_0^t v(z = 0, t') dt'$,

$$\Delta = \frac{4}{3\sqrt{\pi}} \frac{p\sqrt{\nu}}{L\eta} t^{3/2}. \quad (8)$$

Since the accelerated mass is constantly increasing in time, the acceleration \dot{v} decreases with time as $t^{-1/2}$. This leads to the unusual “jerky” increase of the velocity $v(t)$. We note that this predicted motion arises from basic hydrodynamics; it does not depend on the source of the pressure p . We note also that a fixed fraction $\simeq 0.64$ of the input power $p\dot{\Delta}$ goes into kinetic energy; the remainder goes into viscous dissipation.

B. General pressure

Buckling relaxes stress at the tip of the fold; we would, therefore, expect the driving pressure to depend on the displacement. The equation for $\Delta(t)$ can readily be generalized to include such a $p(\Delta)$. We discuss it here for completeness.

$$L\sigma \ddot{\Delta} = p(\Delta) - L\eta \partial_z v|_{z=0}, \quad (9)$$

where the first term on the right is the driving stress, the last term is the stress from the fluid, and σ is the two-dimensional mass density of the sheet. For the fluid, Eq. (1) still applies, and the two are supplemented by a no-slip boundary condition at the interface,

$$v(z = 0, t) = \dot{\Delta}, \quad (10)$$

a condition of vanishing flow far from the surface Eq. (3), and initial conditions of stationarity Eq. (4).

We proceed by eliminating v to obtain an equation for the sheet alone. The velocity Green function of the liquid is given by the boundary condition $v(z = 0, t) = \delta(t)$ and

Eqs. (3) and (4). Explicitly,

$$G(z, t, t') = \frac{1}{2\sqrt{\pi\nu}} \frac{z}{(t-t')^{3/2}} \exp\left(-\frac{z^2}{4\nu(t-t')}\right). \quad (11)$$

The general solution with the no-slip boundary condition of Eq. (10) is obtained simply by integration, $v(z, t) = \int_0^t G(t-t')\dot{\Delta}(t')dt' = \int_0^t G(t-t')\dot{\Delta}(t-t')dt'$. Inserting this expression into Eq. (9) and integrating by parts produces an equation for the sheet alone:

$$L\sigma\ddot{\Delta} = p(\Delta) - \frac{L\eta}{\sqrt{\pi\nu}} \int_0^t dt' \frac{\ddot{\Delta}(t-t')}{\sqrt{t'}}. \quad (12)$$

As before, we may neglect the inertial term on the left-hand side. For a constant pressure, Eq. (12) gives the same displacement as Eq. (7).

C. Application to observed jerks

We may now compare the observed jerk motion with the motion expected from the folding forces. It is straightforward to solve Eq. (12) using the predicted (quadratic) $p(\Delta)$ [30]. The resulting motion proves to be much slower than the observed jerks. We may quantify this discrepancy in two ways. First, we ask what constant pressure p would be required to give the observed displacements Δ in the observed time t . Then we determine the observed kinetic energy and compare it to the energy available from folding.

To find the pressure required to produce the observed jerks, we substitute $\Delta = 2\ \mu\text{m}$ and $t = 0.12\ \text{s}$ into Eq. (12), to obtain $p = 3.2 \times 10^{-3}\ \text{mN/m}$. This is some 50 times larger than the upper-bound folding pressure $p_c = 6 \times 10^{-5}\ \text{mN/m}$ obtained above.

The same discrepancy emerges if we compare the observed kinetic energy E_k with the work W_p done by the pressure difference $p(\Delta)$. Both are proportional to the width w of the jerking region. The pressure $p(\Delta)$ is always smaller than p_c throughout the folding. Thus, $W_p/w < p_c\Delta < 1.2 \times 10^{-13}\ \text{N}$. Other things being equal, the kinetic energy E_k for a given average velocity Δ/t is larger if t is larger (since larger t implies a greater entrained mass). Thus, we may obtain a lower bound on the kinetic energy by limiting t to the observed duration of 0.12 s. For the moment we simply use the constant-pressure solution of Eq. (7) and use

$$E_k/w = L\frac{1}{2}\rho \int dz v(z)^2 = 1.7L\sqrt{\nu t} \left[\frac{1}{2}\rho \left(\frac{\Delta}{t}\right)^2 \right]. \quad (13)$$

We examine this estimate in Sec. IV. For $L = 0.05\ \text{m}$, $\Delta = 2\ \mu\text{m}$, and $t = 0.12\ \text{s}$, this gives $E_k/w = 4 \times 10^{-12}\ \text{N}$ —some 32 times our upper bound of the work W_p supplied by folding. Thus, even when one ignores the work that must go into viscous dissipation, the observed energy is far larger than what the folding energy, W_p , can supply. (Taking account of the dissipated energy, one recovers the factor-50 discrepancy quoted above.)

IV. DISCUSSION

The arguments above indicate a worrisome discrepancy between the observed jerking motion and the mechanics of folding presumed to account for this motion. The discrepancy

is serious; it survives even when we use conservative bounds in our estimates. In this section we survey possible ways to account for the discrepancy. First, we review possible flaws in our description of the kinetic energy and the folding forces. Then we consider other forces that might account for the jerking motions.

Our estimate of the kinetic energy was a simplified one, but it gives a proper lower bound for a given displacement Δ and time t . We will proceed by reinforcing several of the assumptions. First, we assumed a constant pressure, though the actual unbalanced pressure increases with time. However, other choices would have led to a higher kinetic energy. We consider the effect of replacing our constant-pressure estimate by allowing the pressure to increase with time. In order to achieve the required $\Delta (= \int dt \dot{\Delta})$ in the given time t with a time-increasing pressure, we will necessarily reduce $\dot{\Delta}$ at early times and increase it at late times. However, any shift of $\dot{\Delta}$ from earlier to later times has the effect of increasing the kinetic energy. To see this, we consider a small decrease of $\dot{\Delta}$ —denoted $\delta\dot{\Delta}$ —at time $t_<$ over a brief interval Δt . To maintain a fixed total displacement Δ , we make an equal addition to $\dot{\Delta}$ at a later time $t_>$. Any shift of $\dot{\Delta}$ from earlier to later times can be accomplished by repeating this process. This perturbation of $\dot{\Delta}$ creates a corresponding perturbation of the fluid velocity at the final time t : we denote it by $\delta v(z, t)$. We may then express the final kinetic energy $E_k(t)$ in terms of this δv and the initial profile $v_0(z, t)$ using the integral of Eq. (7).

$$\begin{aligned} E_k(t)/w &= L\frac{1}{2}\rho \int dz [v_0(z, t) + \delta v(z, t)]^2 \\ &= E_{0k}(t)/w + L\rho \int dz v_0(z, t)\delta v(z, t) + \mathcal{O}(\delta v^2). \end{aligned} \quad (14)$$

The second perturbing term is necessarily positive provided the (positive) $v_0(z)$ profile is monotonic. To see this we express δv in terms of the Green function G of Eq. (11):

$$\delta v(z, t) = \delta\dot{\Delta}\Delta t [-G(z, t - t_<) + G(z, t - t_>)]. \quad (15)$$

We may express any monotonic v_0 as a sum of positive step functions, each extending from 0 to some Z . For a given step function, the contribution to E_k is given by $\int_{-Z}^0 \delta v$. Thus, it suffices to show that this integral is positive. In terms of the G functions, this means $\int_{-Z}^0 G(z, t - u)$ is an increasing function of u . This may be verified explicitly using Eq. (11). Thus, a small shift in the pressure profile from a constant one to an increasing one with the same Δ and t only increases the energy E_k . If further small shifts are added, the same reasoning implies that the E_k again increases, provided the starting $v_0(z)$ remains monotonic in z . We conclude that the constant-pressure E_k of Eq. (13) under-estimates E_k .

A second assumption that affects our estimate of the kinetic energy is the no-slip boundary condition between the sliding monolayer and the fluid beneath. Having a slip would cause less drag of the fluid and, thus, less kinetic energy. But in our case of hydrophilic heads facing the water, there is no justification for a significant slip.

A further effect that can potentially reduce the kinetic energy is the possibility that the motion is restricted in area, so that less fluid is entrained. As noted above, this restriction

can occur if the surface layer is compressible. The expected compressibility is such that there could be a noticeable effect on the scale of the entire 15-cm sample. To account for this, we assumed that the motion is restricted to a range of only 5 cm. On this scale we argued that any departure from rigid sliding of the sheet would be negligible. One possibility we did not consider is that the modulus of the sheet, Y , is smaller than observed in experiments (that dealt with sheets without any folds). The existence of folds would make the material weaker, softer. If that is indeed the case, the part of the sheet that moves rigidly due to jerking could be smaller. However, in order to resolve the discrepancy, the rigid moving part must be a few millimeters at most, which is not consistent with the statistics of observed jerks [13].

Another potential way to resolve this discrepancy is that we have *under* estimated the folding pressure p . As was noted in Sec. III, the creation of a fold reduces the pressure. Since folding must occur when the pressure exceeds $p_c = 2\sqrt{B\rho g}$, no greater excess pressure can be sustained. This is true even if additional folds are present. Could it be that $p_c > 6 \times 10^{-5}$ mN/m? This would imply that we have greatly underestimated the bending rigidity B . The local structure of the monolayer might imply a bending rigidity greater than is usually observed due to texture in the sheet [31], but how much greater? Equating the folding and kinetic energies requires p_c of at least 2×10^{-6} N/m; i.e., $B > 10^{-16}$ J—a suspiciously larger value.

We do not see how to resolve the kinetic discrepancy discussed here without departing qualitatively from the wrinkle-to-fold model of Ref. [14]. To resolve the discrepancy, either the kinetic energy must be smaller than our conservative bounds or the driving force must be stronger than our bounds. The former possibility seems unlikely. Our estimates for the kinetic energy are based on direct observations of the motion, together with simple and unquestioned hydrodynamics. However, our account of the driving force depends explicitly on the mechanical properties of a folding monolayer leading to the pressure p_c that we estimated. Perhaps this mechanical picture is wrong. What other forces are strong enough to trigger the observed motion? One possible force is the force of adhesion between two folds that touch. These forces are comparable to the surface tension of the fluid and are thus many times larger in magnitude than the pressure p_c . If adhesion forces are responsible, then the observed jerks must take place only after the folds have touched. This leaves unexplained how the folds came to touch and what causes the jerking to stop. A second way to have a larger force is to abandon our picture of a simple molecular monolayer. The observed jerks occur when many folds are already present. The out-of-plane structure from these prior folds could well impart great rigidity to the

surface layer and increase its buckling pressure by a large factor. If such structures were important, it would qualitatively alter our picture of how the jerks occur. There would no longer be a clear connection to the simple wrinkle-to-fold model that gave a plausible account of the jerk displacements.

The force responsible for jerks in the monolayers of Ref. [13] may well be important in a broader context. The wrinkle-fold transition has been implicated in a broader class of nanoscale systems: nanoparticle trilayers [32] and single-component lipid monolayers [3]. The various energies in these systems are different, and the motion is also somewhat different from that of Ref. [13]. Nevertheless, the discrepancy shown above may also apply to these other systems. It is also possible that the force responsible for jerks affects structure as well as dynamics. That is, the magnitude of a fold may be governed by other characteristic lengths than the wrinkle wavelength λ . Still, the incipient instability might be due to the wrinkle-fold mechanism while the rapid subsequent motion is controlled by adhesion or some other force.

This work highlights the distinctive dynamics of thin solid sheets on fluids in general. Equation (12) applies whenever such a sheet is accelerated by an unbalanced force, whether folding occurs or not. The equations imply a distinctive form of acceleration and a distinctive partitioning of the supplied work into kinetic energy and dissipation.

V. CONCLUSION

The wrinkle-to-fold mechanism [14] for thin film buckling has allowed a new avenue for understanding buckling phenomena in a range of nanoscale systems. Its successes in explaining structural aspects of folding have led us to apply it to the well-studied dynamics of monolayer jerks. For these dynamic phenomena, our study indicates that other forces are at play. Supporting this conclusion are experiments on lipid-coated micro-bubbles, where it is clear that gravity, an important ingredient of the folding mechanism, plays no role [12,15]. These other forces must be much stronger than those previously considered. The necessity of such forces underscores the remarkable nature of monolayer jerks. It also raises the importance of understanding these jerks.

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